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Graphite an exfoliated and organomodified filler for polymeric nanocomposites

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Abstract

Two types of graphite were processed using mechanical route to obtain the highest possible exfoliated graphite. Using three various media, commercial dishwashing liquid, mixture of defined concentration of 4 ammonium quaternal salts and single salt hexadecyl trimethylammonium bromide with addition of ethylene glycol, the liquid exfoliation shear-forces process was employed. The process provides defined exfoliated particles with small particles size and greater crystallinity compare to original graphite. Exfoliated particles were tested using scanning electron microscopy and atomic force microscopy to explain the shape and morphology changes at shearing forces process. The particles were found as irregular rounded shapes with tiny crystals of used organic matter on the edges of particles. Such modification brings advantage for utilization exfoliated particles in polymeric nanocomposites because they will be more likely interacting with organic substance.

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Keywords: Graphite; exfoliation; organic modification; particles morphology; structural properties.

1. Introduction

Applicability of countless nanoparticles for improvement countless of matrices is hot topic for materials research and development, though nanotechnology brings new options for products prepared via nanofiller utilization. One of

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the wide ranges of nanoparticles is layered materials. Layered materials consist of two-dimensional platelets weakly stacked to form three-dimensional structures. The archetypal example is graphite, which consists of stacked graphene monolayers. Over the past decade, many methods have been developed to exfoliate layered graphene materials to produce monolayer nanosheets of graphene. Such exfoliation creates extremely high-aspect ratio nanosheets with enormous surface area, which are ideal for applications that require surface activity. More importantly, however, the two-dimensional confinement of electrons upon exfoliation leads to unique optical and electrical properties [1-3].

Exfoliation of graphite for the purpose to obtain in ideal case the individual graphene layers is nowadays method number one. The most popular and used in industry is Hummers method in which raw graphite powder are oxidized using potassium permanganate ($KMnO_4$) in acidic solution [4]. This method gives relatively high yield of oxidized graphene (GO - graphene oxide). The GO material consists of graphene-like sheets, chemically functionalized with compounds such as hydroxyls and epoxides, which stabilize the sheets in water. Functionalization disrupts the electronic structure of graphene. GO is an insulator rather than a semi-metal and is conceptually different from graphene. Defect free graphene is generally produced by graphite powder sonication either in certain solvents [5-7] or aqueous surfactant [8-10] solutions. Although the functional groups can be removed by reduction, so far this leaves a significant number of defects, which continue to disrupt the electronic properties remain. The sonication tends to break up the graphite crystallites as well as exfoliating them to give large number of graphene nanosheets [11].

Graphene-like nanoparticles have wide range of application based on their properties [12-14].

In this study the aim is to prepare uniform particle size of exfoliated graphite via mechanical methods using shearing force of kitchen blender with help of surfactants. The morphology of particles is one of the parameters observed. Three surfactant solutions are being compared for exfoliated graphite particles yield. Methods as X-ray powder diffraction, particle size distribution evaluation and microscopy for morphology imaging are used to explain the effect of exfoliation. The purpose of exfoliated particle preparation is to use it in polymeric matrix where the optimal dispersion should be obtained at low percentage of filler.

1.1. Materials and equipment

The studied materials are two types of graphite flaky (Grf) and powdered (Grp) used for industrial purposes, well crystalline (Fig.1), mean particle size 360 μm and 240 μm, respectively. The organic liquid media for mechanical exfoliation were prepared from: Ethylene glycol (CH_2OH) (Sigma Aldrich), dodecyltrimethyl ammonium bromide (M = 308.35 g.mol^{-1}) ($C_{15}H_{34}BrN$), (FLUKA), dimethyldioctadecyl ammonium bromide (M = 630.96 g.mol^{-1}) ($C_{38}H_{80}BrN$), (FLUKA), Cetyltrimethylammonium bromide (M = 364.45 g.mol^{-1}) ($C_{19}H_{42}BrN$), (FLUKA) and trihexyltetradecyl phosphonium bromide (M = 563.76 g.mol^{-1}) ($C_{32}H_{68}BrP$), (FLUKA). Dishwashing liquid JAR (Procter and Gamble, Czech Republic) was used as it purchased. The main tool for graphite exfoliation was kitchen blender Gorenje (max.2000 rpm, 600W) with glass jar. Paper filter 100 μm pores.

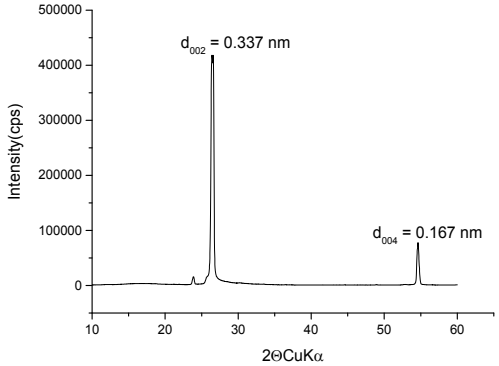


Fig. 1. XRD pattern of original flaky graphite Grf with denoted basal diffractions.

1.2. Sample preparation

The preparation method for exfoliated graphite was adopted from very popular work of Varrla et al. [3], where ordinary kitchen blender was employed to prepare defect free few layer graphene nanoparticles. The amount of 20 g original graphite was always immersed in 500 ml of one of the aqueous solutions. With help of common dishwashing liquid (20 g in 500 ml), the graphite powder was exfoliated in blender (mixing conditions 45 min mixing and each 5 min break for 1 min, laboratory condition). Mixed graphite in liquid was filtrated using 100 μm pores paper filter, where filtrate contained the smallest particles. Drying of filtrate was done in furnace at 120 °C for 24 h on large Petri dish.

For following experiment two solutions of selected defined surfactants were prepared. First aqueous solution of concentration c = 0.025 mol.dm^{-3} of each substance: dodecyltrimethylammonium bromide, cetyltrimethylammonium bromide, trihexyltetradecylphosphonium bromide and dimethyldioctadecylammonium bromide was prepared and mixture in ratio 2:2:1:1, respectively, blended, where the concentration is selected based on molecular weight of substance (higher molecular weight lower quantity in mixture). The mixture of surfactants with the variable length of the aliphatic chains of hydrocarbons was set to mimic the commercial product, dishwashing detergent, but not to make the solution very complex. Therefore, only ammonium salts were selected.

Second solution of cetyltrimethylammonium bromide of concentration c = 0.05 mol.dm^{-3} with 1ml of ethylene glycol in 500 ml of solution was prepared. In this case single ammonium salt was used and ethylene glycol was added to bring a stearic effect for solution.

The same procedure was repeated for the exfoliation of graphite using both above mentioned solutions.

Samples originated from the three suspensions were denoted as following: Grf/J and Grp/J for method with dishwashing liquid JAR; Grf/4S and Grp/4S for method with mixture of four various surfactants; Grf/1S and Grp/1S for method with one surfactant solution.

1.3. Characterization methods

The X-ray diffraction (XRD) analysis was carried out on the X-ray diffractometer Ultima IV (RIGAKU, Japan). The XRD patterns were recorded on the powder samples pressed on the glass slide in the symmetrical Bragg-Brentano diffraction geometry in the 8 - 80° 2θ range under CuKα radiation (λ = 0.1541 nm) and the scintillation counter detector with a scanning rate of 2°/min at 40 kV and 40 mA.

The particle size (PS) and particle size distribution (PSD) was determined by the HORIBA Laser diffraction particle size analyzer (LA-950 instrument) with a two short-wavelength blue and red light source in conjunction with forward and backscatter detection.

Scanning electron microscope Philips XL30 (Nederland) and Regulus Hitachi (Japan) were used for viewing morphology of powdered samples. Samples were analyzed as received from experiment. Scanning conditions mentioned in figure 4 captions.

Atomic force microscopy Solver Next was used for visualizing particles of exfoliated graphite; the scanning conditions were at room temperature using non-contact mode and 10 x 10 μm scanner.

2. Results and discussion

Obtained samples were characterized for structural parameters, size and morphology.

2.1. Characterizations of exfoliated graphite crystallinity

The important characteristic of material is structural analysis where crystallinity is one of the more pronouncing. In case of exfoliated graphite XRD analysis was performed to obtain information about level of destruction of original graphite material. Both graphitic materials shown changes in diffraction pattern after mechanical exfoliation in liquids. However, the substances originated from ionic surfactants are present in the exfoliated graphite powder

and patterns are influenced by intensive and very sharp peaks. The graphite peak is visible as broadened 002 diffraction in all cases (Fig. 2).

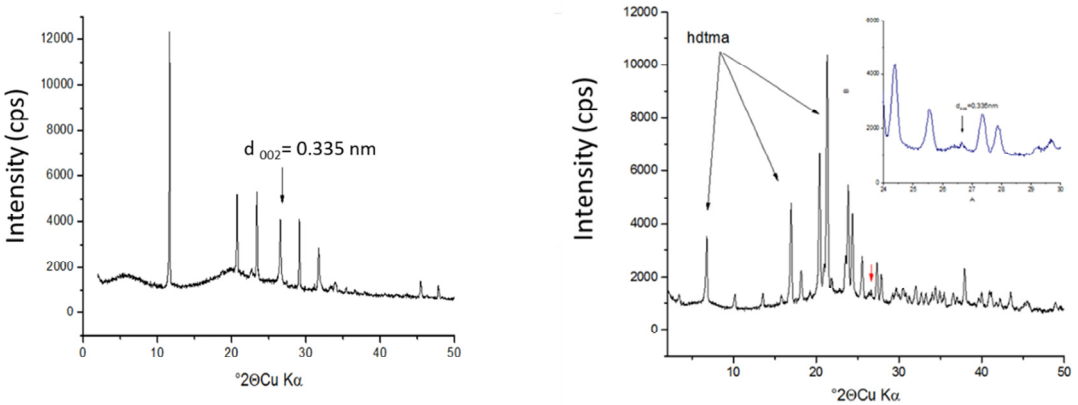


Fig. 2. XRD patterns of: (a) Grf/J and organics form dishwasher liquid; (b) Grf/1S and hexadecylamonium bromide (hdtma). Graphite 002 basal diffraction is marked with arrow and rest of the peaks in pattern belongs to organic matter.

Evaluating the mean particle size decrease there is no extreme differentiation among individual exfoliated powders (Table 1). Nonetheless the blended suspension passed through filter with 100 μm pores, based on distribution curve value D_{90} was obtained mostly higher than 100 μm and the highest for particles obtained using one sufractatnt solution. The smallest particles where obtained for both graphites, powder and flake, using method with dishwasher detergent. Smaller average value was observed for flaky graphite using mixture four of surfactants, but the same solution used for the powder graphite didn't give the same low value, therefore there is no prove that such mixture is the most suitable for obtaining best results.

Table 1. List of original graphites and prepared samples of exfoliated graphites.

Sample	Mean (μm)	D_{10} (μm)	D_{90} (μm)	L_c (nm)	FWHM (2Θ)	SSA ($m^2.g^{-1}$)
	Particle size					
Grf	336	201	526	16	0.49	54
Grp	260	158	401	15	0.42	58
Grf/P	***70***	10	160	22	0.38	41
Grp/P	***70***	14	120	19	0.38	41
Grf/4S	57	17	89	23	0.29	38
Grp/4S	87	21	179	16	0.37	53
Grf/1S	90	29	190	***22***	0.40	48
Grp/1S	84	43	143	***20***	0.36	44

As following structural changes of exfoliated graphite's were evaluated. The XRD methods helped to explain effect of exfoliation on graphite. Mean crystallite size at direction perpendicular to graphene layers L_c was calculated according Williamson and Hall approach [15]. It is evident that crystallite size of exfoliated filtrated particles is growing from approx. 15 nm to average 20 nm (Table 1). Such a growth should be caused by redefining of blended particles via filtration. As it was mentioned before, the mechanical liquid contributing to exfoliation is a technique for defect-free graphene preparation. Therefore, the particles in average present higher crystallinity than original graphite; equally for both types of graphite.

Another parameter calculated using XRD methods is specific surface area (SSA). All exfoliated samples were found to have lower SSA than original graphites. Better defined exfoliated particles will provide lower surface.

2.2. Morphology and topography of exfoliated particles

The morphology of prepared particles was observed using scanning electron microscopy (SEM) to receive information how the process of mechanical exfoliation in liquids changed the rigid graphite particles. In the process several forces are induced. First, it is vortex force causes by blades created turbulence of liquid. Another is the shearing force accompanied with cutting effect of blades of blender.

Thanks to shearing and cutting forces of blender blades the exfoliated particles have uneven edges of flakes, as it was observed using SEM (Fig.4). The particles are not only exfoliated, as a very well visible in case of Grf/J in Fig. 4b, but they are elongated. We presume that they were shaped by blender blades cutting and rounding the graphite platelets. In case of Grf/J we can see nicely decorated edges of exfoliated graphite by crystals of organic matter (Fig. 4b white dots).

Topography of exfoliated particles correlates with findings from SEM images. As example we selected data of Grf/J (Fig. 3), where flat particles with cascade-like character of exfoliated particles are presented.

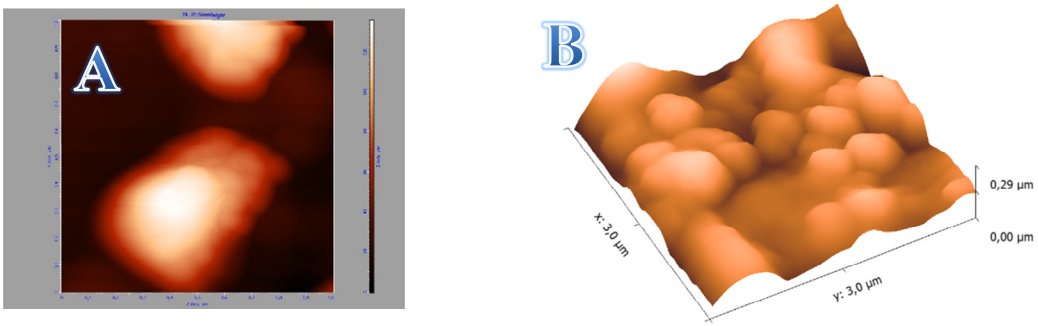
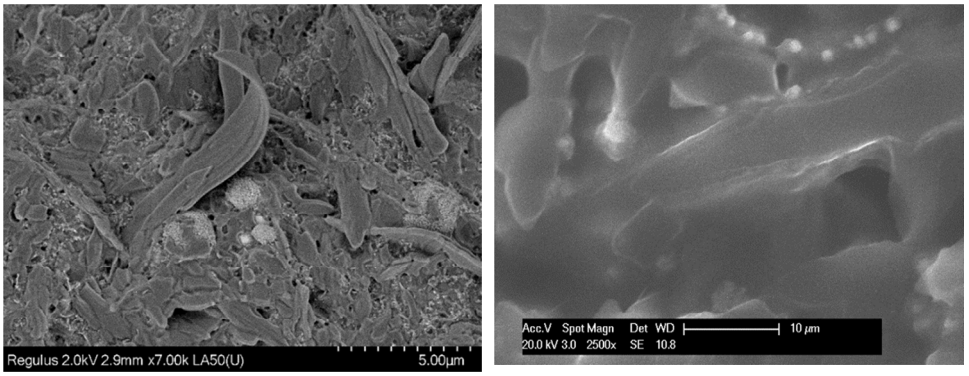


Fig. 3. Atomic force microscopy images of exfoliated graphite Grf/J: (a) 2D view, (b) 3D view where hight of particles is below 300 nm.



a) b)

Fig. 4. Scanning electron microscopy images of exfoliated graphites: (a) Grf/1S; (b) Grf/J.

3. Conclusion

Two types of graphites, flaky and powdery, were undergoing exfoliation using mechanical shearing force process with help of ionic liquids. Methods employed kitchen blender and 3 types of ionic solutions.

The effect of presented method was very successful to bring radically smaller particles with well-defined particles size. However, there was no evidence to find differences among the type of solution since all selected surfactants solution gave comparable results. The same we can conclude for type of graphite. Both flaky and powdery graphite were finally exfoliated in comparable manner giving similar shape and size of the exfoliated particles.

Positive finding out of this study is the fact that particles are not only delaminated and exfoliated but also their shape is changed due to cutting forces of blender blades, providing irregular shapes of particles.

Since there is no reactive condition in the blender for graphite and organics to create bonding interaction, the small crystals grown on the edges of flakes would be attached to the surface by physical or weak forces and stable only at form of the solid state. This relatively nonbonding modification might be very useful in case of utilization exfoliated particles of graphite in polymeric nanocomposites. In case of immersion of such modified particle in the monomer or, in melt approach of compounding, in polymer, the predisposition of organo-inorganic carbon particle to merge with organic matter will be higher than in case of pure inorganic graphite. The advantage of irregular shape of particles will be in better interaction with matrix.

We can summarize that presented method can provide uniform small particles (in average below 80 μm) with relatively stable crystallite size (about L_c = 20 nm) with beneficial irregular shape and modified surface with anchored crystallized organic matter.

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References

[1] J. N. Coleman M. Lotya, A. O’Neill, S. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grieveson, K. Theuwissen, D. W. McComb, P. D. Nellist, V. Nicolosi, Science 331 (2011) 568-571.

[2] V. Nicolosi, M. Chhowalla, M. G.Kanatzidis, M. S. Strano, J. N. Coleman, Science 340 (2013) 1226419-18.

[3] E. Varrla, K. R. Paton, C. Backes, A. Harvey, R. J. Smith, J. McCauley, J. N. Coleman Nanoscale 6 (2014) 11810-11819.

[4] W. S. Hummers, R. E. Offeman, J. Am. Chem. Soc. 80 (1958) 1339-1339.

[5] D. J. Finn, M. Lotya, G. Cunningham, R. J. Smith, D. McCloskey, J. F. Donegan, J. N. Coleman, J. Mater. Chem. C 2 (2014) 925-932.

[6] F. Torrisi, T. Hasan, W. P. Wu, Z. P. Sun, A. Lombardo, T. S. Kulmala, G. W. Hsieh, S. J. Jung, F. Bonaccorso, P. J. Paul, D. P. Chu, A. C. Ferrari, ACS Nano 6 (2012) 2992-3006.

[7] B. Mendoza-Sanchez, B. Rasche, V. Nicolosi, P. S. Grant, Carbon 52 (2013) 337-346.

[8] J. M. Englert, J. Röhrl, C. D. Schmidt, R. Graupner, M. Hundhausen, F. Hauke, A. Hirsch, Adv. Mater. 21 (2009) 4265-4269.

[9] M. S. Kang, K. T. Kim, J. U. Lee, W. H. Jo, J. Mater. Chem. C 1 (2013) 1870-1875.

[10] M. Lotya, Y. Hernandez, P. J. King, R. J. Smith, V. Nicolosi, L. S. Karlsson, F. M. Blighe, S. De, Z. M. Wang, I. T. McGovern, G. S. Duesberg, J. N. Coleman, J. Am. Chem. Soc. 131 (2009) 3611-3620.

[11] Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari, J. N. Coleman, Nature Nanotechnology 3 (2008) 563-568.

[12] M. Yi, Z. Shen, J. Mat. Chem. A 3 (2015) 11700-11715.

[13] J.Pang, A. Bachmatiuk, I.Ibrahim, L. Fu, D. Placha, G. S. Martynkova, B. Trzebicka, T. Gemming, J. Eckert, Mark H. Rümmeli, J. Mater. Sci. 51 (2016) 640-667.

[14] M. Šupová, G.S. Martynková, K. Barabaszová, Sci. Advanced Mater 3 (2011) 1-25.

[15] G. K. Williamson, W. H. Hall, Acta Metall. 1 (1953) 22-31.